Tellus (1980), *32*, 299–300

SHORT CONTRIBUTION

The ozone layer—uncertainties in reaction rates

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(Manuscript received November 2; in final form November 26, 1979)

The concern about possible modifications to the ozone layer due to man's activities has prompted a number of numerical model predictions of the behaviour of atmospheric ozone. All models contain approximations, and it is important to consider the model predictions in the light of these approximations. Apart from the purely numerical approximations, uncertainties in the treatment of atmospheric chemistry, radiation and dynamics can be identified. See for instance Mahlmann (1975) and Harwood and Pyle (1979). The impact of recent evaluations of reactions involving HO_2 was discussed by Crutzen and Howard (1978) and Whitten et al. (1978).

In this note we will discuss briefly the importance to calculations of the ozone layer of the rate constants of the reactions:

$$O(^3P) + O_3 \rightarrow 2O_2 \quad k_1 \tag{1}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad k_2 \tag{2}$$

(M = third body collision partner)

recently determined by Arnold and Comes (1979).

The finding that the reactions of oxygen and its allotropes alone (the so-called Chapman reactions) could not adequately explain the observed amounts of ozone leads to the conclusion that oxides of hydrogen, nitrogen and chlorine also play a role in the photochemistry of atmospheric ozone. Numerical models that include these species seem to confirm that such a photochemical scheme is sufficient to reproduce numerically the observed distributions of ozone and its seasonal variations. However, the rate constants for the two above mentioned Chapman reactions recently determined by Arnold and Comes differ from those currently used in models.

Their new rates are:

$k_1 = (2.12 \pm 0.18) \times 10^{-11} \exp[-(2337 \pm 26)/T]$ cm^3 molec^{-1} s^{-1},

$k_2^{Ar} = (6.24 \pm 1.53) \times 10^{-35} \exp[(525 \pm 70)/T]$ cm^6 molec^{-2} s^{-1},

$k_2^{O_2} = (6.75 \pm 0.43) \times 10^{-35} \exp[(635 \pm 18)/T]$ cm^6 molec^{-2} s^{-1},

$k_2^{N_2} = (1.82 \pm 0.23) \times 10^{-35} \exp[(995 \pm 37)/T]$ cm^6 molec^{-2} s^{-1}.

The recommended rate constants (Garvin and Hampson, 1978) used in various models (called "old rates" in the figure) are

$k_1 = 1.9 \times 10^{-11} \exp(-2300/T)$ cm^3 molec^{-1} s^{-1}

$k_2 = 6.6 \times 10^{-35} \exp(510/T)$ cm^6 molec^{-2} s^{-1}

for M = Ar,

with a relative efficiency of 1.6 and 1.7 for N_2 and O_2, respectively.

We have used the new rate constants in the two-dimensional time-dependent model developed at the Department of Atmospheric Physics, University of Oxford (Pyle, 1977, Pyle, 1979). As an example of the results obtained, total ozone amounts versus latitude are shown in Fig. 1. The comparison with results obtained with the "old reaction rates" shows that significantly higher total ozone values are obtained with the new rate constants, an increase of up to about 10% at high latitudes. The dotted curve shows zonally-averaged total ozone values from satellite and ground-based measurements for comparison (Prior and Oza, 1978). In view of the large natural variability the agreement of the measured and predicted meridional distribution of total ozone is reasonable. The model tends to overestimate in the tropics and underestimate in high northern latitudes.

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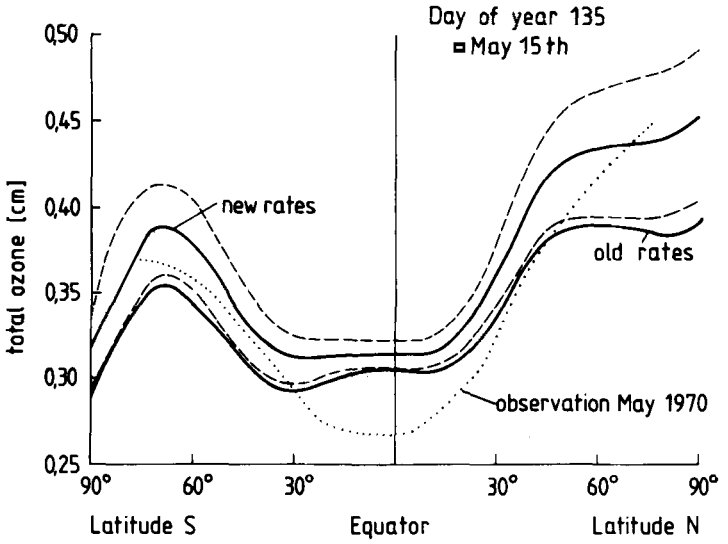

Fig. 1. The total ozone vertical column in atm-cm versus latitude computed for May 15th with the 2-D Oxford model. The solid curve labelled "old rates" is obtained by using presently recommended rate coefficients for reactions (1) and (2). The curve "new rates" includes rate coefficients recently measured by Arnold and Comes (1978). The two dashed curves result from taking into account the most extreme uncertainty ranges of the new data. The dotted curve shows zonally averaged total ozone content from IRIS, BUV satellite and Dobson ground-based measurements (Prior and Oza, 1978).

We have also studied the influence of the uncertainty ranges of the new reaction rates. The "best" and "worst" cases have been assessed by combining the upper limit of k_1 with the lower limit of k_2 and vice versa. The results for these extreme cases are plotted in the figure as dashed lines. An increase in model ozone results in either of these extreme cases. Thus uncertainty in these important reaction rates adds further uncertainty to model predictions of ozone depletion.

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